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Influence of magnetic field on Cr(VI) adsorption capability of given anaerobic sludge

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Abstract To provide beneficial guide for the application of the magnetic field in the bio-treatment of the Cr(VI)-contained wastewater, sludge samples from the control bio-system A (absent of magnetic field) and the contrast bio-system B (present of magnetic field) were used to adsorb the synthetic wastewater with 100 mg l^{-1} Cr(VI). Influences of two adsorption modes, single adsorption and once continuous adsorption, on the Cr(VI) adsorption capacities of both sludge samples were compared. And the influence of regeneration on the Cr(VI) adsorption capacities were also studied. The results of adsorption experiments showed that the Cr(VI) adsorption capacities of the first single adsorption for sludge sample A and B were pretty nearly, which were 9.79 and 9.93 mg, respectively. And after 5 single adsorption periods, the total Cr(VI) adsorption capacity and efficiency of the sample B were 25.88 and 55.66 mg Cr(VI) g^{-1}VSS, while those of the control were 14.95 and 33.98 mg Cr(VI) g^{-1}VSS, respectively. For the sludge sample A and B after a single adsorption, both functions of regeneration were remarkable. But after 13 cycles of the single adsorption-regeneration, the Cr(VI) adsorption capacity and efficiency of the sample B were 110.15 and 189.91 mg Cr(VI) g^{-1}VSS, while those of the control were 70.89 and 140.38 mg Cr(VI) g^{-1}VSS, respectively. Though the Cr(VI) adsorption capacity of a once continuous adsorption period was more than that of a single adsorption period obviously, the Cr(VI) removal rates of the sludge sample A and B in the third period of once continuous adsorption-regeneration were only 8.12 and 33.51%, respectively. It was concluded that the weak magnetic field did improve the Cr(VI) bio-removal efficiency and the sludge stability, the batch treatment was an ideal operation mode for the bio-treatment of the Cr(VI)-contained wastewater, as compared with the continuous operation mode, but regeneration and enough sludge content were two necessary conditions to ensure the efficiency of batch treatment.

Keywords Magnetic field · Adsorption · Anaerobic sludge · Cr(VI)

Abbreviations

COD_{Cr}	Chemical oxygen demand
Cr(VI)	Hexavalent chromium
F/M	Organic load
MLSS	Mixed liquor suspended solids (g l^{-1})
VSS	Mixed liquor volatile suspended solids (g l^{-1})
SVI	Sludge volume index (l g^{-1})
SV_{30}	Sludge volume (%)
CFU	Colony forming unit

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Introduction

Chromium is widely used in electroplating, leather tanning, metal finishing and chromate preparation, which exists in two stable oxidation states Cr(III) and Cr(VI). The Cr(VI) state is concerned particularly because of its toxicity. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to humans. Strong exposure of Cr(VI) causes cancer in digestive tract or lung and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage (Shakoori et al. 2004). Cr(VI) causes two types of dermatological toxicities: allergic contact dermatitis (ACD) and skin ulcers. Repeated exposure to Cr(VI) in concentrations of 0.004–0.025 mg l^{-1} can induce sensitization and elicit chromium ACD. Exposure to 0.020 mg l^{-1} Cr(VI) can cause skin ulcer in non sensitized people. Some investigators recommend reducing Cr(VI) concentrations in consumer products, such as detergents, to less than 0.005 mg l^{-1} (Shelnutt et al. 2007). Hence, it becomes imperative to remove Cr(VI) from wastewaters before discharging them into aquatic systems or onto land.

Different methods, such as reduction-precipitation, ion exchange, electrodialysis, reverse osmosis, solvent extraction, electrochemical precipitation and adsorption, have been suggested for the removal of Cr(VI). As compared, bio-removal of Cr is becoming one of the hottest research fields for its merits of high efficiency, low cost and safety. Presently, accumulation of heavy metals by microbe is a widely concerned phenomenon, and toxic metals removal or valuable metals enrichment and regeneration from industrial wastewater by living or abiotic biomass are also one of the most interesting research fields (Ferraz et al. 2004).

Many biotic pure and mixed microbial cultures isolated from chromium-polluted areas have been investigated for the bioaccumulation properties of Cr(VI) (Srinath et al. 2002; Lameiras et al. 2008). Camargo et al. isolated 16 Chromium-resistant bacteria (CRB) from soil samples obtained from Brazil and US and identified them by 16S rRNA gene sequencing. Ten of the isolates were bacterial species that had never been reported as CRB. Most of the isolates belonged to the *Bacillaceae* family and *Actinomicetales* order, respectively (Camargo et al. 2005). The mechanism of "adsorption-coupled reduction" was concluded first by Park et al. and was widely accepted as the mechanism of Cr(VI) biosorption by abiotic biomaterials such as fermentation waste of *Corynebacterium glutamicum*, the protonated biomass of brown seaweed, *Ecklonia*, dead biomass of four fungal strains—*Aspergillus niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae* and *Penicillium chrysogenum* (Park et al. 2005, 2008a, b).

It was proved that natural magnetite and its sediment could accelerate the reduction of Cr(VI) by monitoring the ratio of $^{53}Cr/^{52}Cr$ in natural water (Ellis et al. 2002). As an effective method, magnetic separation technique had been applied to the treatment of many wastewaters, such as oil-bearing effluent, mine effluent (Karapinar 2003). The application of magnetic field in wastewater treatment systems could improve the degradation of organic matters by magnetizing wastewater and producing strong oxidant such as H_2O_2, which was an promising technique with low energy demand, easy operation, non-secondary pollution and low cost (Hu et al. 2006). Recently, based on the functions of magnetic separation and bio-removal, magnetite immobilized enzyme and cells were testified an increase of pollutant removal efficiency (Bayramoglu and Arica 2008). For example, the bio-functional magnetic beads, which were constituted by the powder of *Rhizopus cohnii* and Fe_3O_4 particles coated with alginate and polyvinyl alcohol (PVA), could adsorb and recover Cr(VI) from liquid, and the magnetic separation technology would make their separation more convenient (Li et al. 2008a).

To improve cell accumulation capability, researchers have taken several methods, such as screening high-efficiency strains, altering morphological and physiological features by genetical manipulation (Zouboulis et al. 2004). A survey of literature indicated that not much work had been done so far on magnetic field for the bio-treatment of the Cr(VI)-contained wastewater. Based on the previous studies of Cr(VI)-bio-adsorption in magnetic ASBR (anaerobic serial batch reactor), to further evaluate the Cr(VI) adsorption capability and the sludge stability and offer guidance to the practical operation, the paper aimed to investigate the influence of some magnetic field on the adsorption capability of the sludge on Cr(VI) by comparing with a control from the viewpoint of adsorption mode and sludge regeneration.

Experimental materials

Strains and sludge for tests

Strain A (*Brevibacillus* sp.) and B (*Bacillus* sp.) are two bacteria with high removal efficiency of Cr(VI), which were screened in the previous researches (Deng et al. 2004; Xu et al. 2005b; Xu and Sun 2005, 2008).

Sources and qualities of Cr(VI) contained wastewater

Synthetic wastewater I that is made of potassium dichromate contains some nutrients and supplements, such as glucose, KH_2PO_4, $MgSO_4$ and trace metals. The water qualities are 60 mg l^{-1} of Cr(VI), 180 mg l^{-1} of COD_{Cr} and 6.6 of pH value. The concentration of nutrient N and P was controlled according to the ratio of 100:6:1 (COD_{Cr}:N:P). This kind of wastewater was used in system running.

Synthetic wastewater II is prepared by potassium dichromate containing Cr(VI) of 100 mg l^{-1} and used in Cr(VI) bio-adsorption experiments.

Nutrient liquid for regeneration

The nutrient liquid is the synthetic wastewater I with absence of Cr(VI)

Test devices

The test devices were two anaerobic serial batch reactors (ASBR) with the same specs—20 cm (length) × 20 cm (breadth) × 55 cm (high). The MLSS of both systems was 3,000 mg l^{-1}, and the anaerobic sludge was stirred slowly in the reactors by mixture-returning at the flux of 83.3 ml min^{-1}. The magnetic powder was magnetized to form an average magnetic density of 6.0 mT and added into the reactor B at a mass ratio of magnetic powder: MLSS = 1:1, meanwhile, a magnetic field was put on to avoid the fade away of magnetism and supply an constant magnetic field to the reactor B, which was realized by setting the magnetic pieces (Φ80 mm × 1 mm) into the reactor B. The introduction of the magnetic pieces could provide a magnetic field of 0–4.5 mT between pieces (as showed in Fig. 1). As a control, there was no magnetic powder and magnetic pieces in the reactor A. The sludge characteristics of both reactors and the influence of magnetic powder on the sludge characteristics of the reactor B was showed in Table 1.

The duration of each ASBR operation units, such as wastewater inflow, anaerobic reaction, sludge sedimentation, water discharge and system unused were 0.5, 10, 12, 0.5, 1 h, respectively.

Magnetic powder and magnetic pieces

The magnetic powder is Fe_3O_4 of 10 μm in granularity, and the magnetic pieces with a surface magnetic density of 0–6 mT are round in shape with 8.0 cm in diameter and 1 mm in thickness, which is ferrite magnet embodied rubber. Both the magnetic powder and pieces were purchased from GuangZhou Magnetic Material Factory.

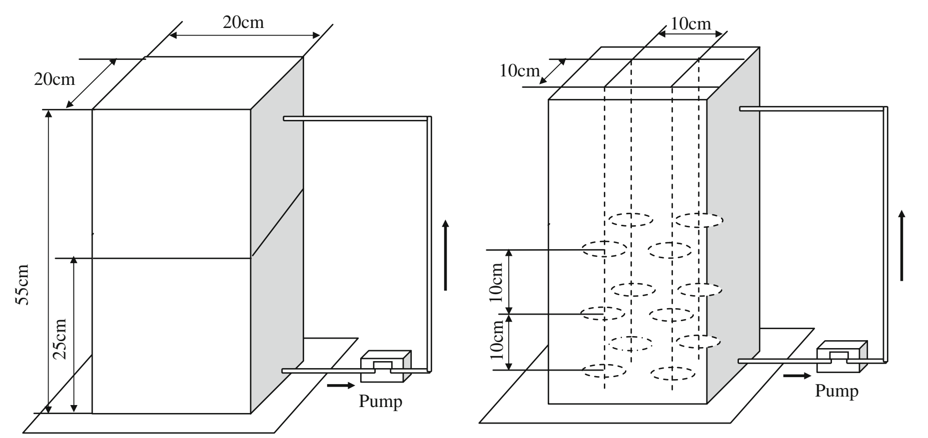

Fig. 1 Sketch maps of the test devices

Table 1 Characteristics of the activated sludge in the reactors A and B

Sludge	Index				
	SV_{30} (%)	SVI ($l\ g^{-1}$)	MLSS ($g\ l^{-1}$)	Ash constituent (%)	VSS ($g\ l^{-1}$)
A	38.0	33.3	11.4	41.5	6.80
B					
I[a]	39.0	32.2	12.1	42.2	7.00
II[b]	41.5	28.4	14.6	41.4	8.75

[a] Before the addition of magnetic powder

[b] After the addition of magnetic powder

Experimental methods

Determination of Cr(VI) and magnetic density

Cr(VI) was detected by Diphenyl Carbazide Method. 1,5-diphenyl carbazide forms a pink complex in the presence of Cr(VI) ions in acidic solutions. The concentration of Cr(VI) was calculated from absorbance at 540 nm using UV spectrophotometer after a 30-min-sedimentation.

The magnetic density was determined by platform tesla-meter PF-035-2 (produced by Litian Magneto-electrican Science and Technology LTD.).

Determination of the optimum adsorption time

Fourteen beakers of 500 ml were charged with 100 ml of testing sludge, which was a mixed sludge from the reactor A and B according to the volume ratio of 1:1. The supernatant liquid was thrown away after a 30-min-sedimentation and 100 ml synthetic wastewater II was added into each beaker. All the 14 beakers were set in a thermostat magnetic stirring apparatus in 7 groups and agitated slowly at 150 rpm. The adsorption initial pH and temperature was 6.6 and 25°C, respectively. Adsorption reaction was stopped by taking out two beakers (a group) from the stirrer at the stirring time of 15, 20, 30, 45, 60, 90, 120 min, respectively. And the supernatant liquid was collected carefully and the residual Cr(VI) content was determined after a 30-min-sedimentation. Cr(VI) removal rates of each group (2 replicates) were averaged and applied to get the curve on the variation of Cr(VI) removal rates with the stirring time.

Determination of single adsorption capacity

According to the adsorption method and the optimum adsorption time screened by the experiment forementioned, the testing sludge samples from the reactor A and B were used to adsorb the Cr in 100 ml of the synthetic wastewater II, respectively. There were three replicates for each sludge samples, considering not only the test error, but also the influence of too much samples on the stable operation of the sludge system. After a 30-min-settlement, Cr(VI) content in the supernatant liquid was determined and calculated to get the value of single adsorption capacity. Cr(VI) adsorption capacity of a single adsorption period (q_{Cr}) could be calculated according to the formula 1:

$$q_{Cr} = (C_1 - C_2) \times V \quad (1)$$

In which, q_{Cr}, Cr(VI) adsorption capacity of the single adsorption period (mg); V, the volume of the supernatant liquid for the single adsorption (L); C_1 Cr(VI) concentration of the supernatant liquid before stirring (mg l^{-1}); C_2, Cr(VI) concentration of the supernatant liquid after stirring (mg l^{-1}).

Cr(VI) adsorption efficiency of the sludge sample for a single adsorption period (e_{Cr}) could be calculated according to the formula 2:

$$e_{Cr} = (C_1 - C_2) \times V/m = q_{Cr}/m \quad (2)$$

In which, m, the mixed liquor volatile suspended solids of the sludge sample (gVSS).

Determination of once continuous adsorption capacity

Once continuous adsorption capacity is the sum of the Cr(VI) adsorption capacities of several periods of the single adsorption experiments which were done continuously for the same sludge sample. The single adsorption capacity was the quality of Cr(VI) within each 100 ml of the synthetic wastewater II adsorbed by a testing sludge sample from the reactor A or B. The first single adsorption period began when the first 100 ml of the synthetic wastewater II was added into the beaker and mixed with the sludge sample, and ended when the supernatant liquid was discharged after a 30-min-settlement, the single adsorption capacity of the first period could obtained according the formula 1. The second 100 ml of the synthetic wastewater II was added into the beaker and mixed with the same sludge sample, and ended when the supernatant liquid was discharged after a 30-min-settlement, the single adsorption capacity of the second period could also obtained. Then carried on the third and the forth single adsorption period, and so on. The single adsorption period held on in succession until the solution reached equilibrium, when was considered as a once continuous adsorption period. There were 3 replicates for each sludge samples, considering not only the test error, but also the influence of too much samples on the stable operation of the sludge system. The once continuous adsorption capacity (Q_{Cr}) of Cr(VI) could be calculated according to the formula 3:

$$Q_{Cr} = \sum q_i = \sum (C_{i1} - C_{i2}) \times Vi \quad (3)$$

In which, Q_{Cr}, Cr(VI) continuous adsorption capacity (mg); q_i, Cr(VI) adsorption capacity for the i-th time of the single adsorption period (mg); V_i, the volume of the supernatant liquid for the i-th single adsorption period (L); C_{i1}, Cr(VI) concentration of the supernatant liquid before stirring of the i-th single adsorption period (mg l^{-1}); C_{i2}, Cr(VI) concentration of the supernatant liquid after stirring of the i-th single adsorption period (mg l^{-1}).

Cr(VI) adsorption efficiency of the sludge sample for a once continuous adsorption period (E_{Cr}) could be calculated according to the formula 4:

$$E_{Cr} = \sum q_i/m = \sum (C_{i1} - C_{i2}) \times Vi/m = Q_{Cr}/m \quad (4)$$

In which, m, the mixed liquor volatile suspended solids of the sludge sample (gVSS).

Influence of regeneration on Cr(VI) adsorption capability

The previous researches showed that Cr(VI)-adsorbed sludge could be regenerated by leaving unused with some nutrient liquid for over 20 h (Xu et al. 2005a). The single adsorbed and the continuous adsorbed sludge samples were regenerated with the nutrient liquid for 48 h and then carried on the next adsorption period until any sludge sample showed the status of adsorbing saturation obviously. The adsorption capacities of the testing sludge samples for each adsorption period were determined and calculated, which were summed up to get the total Cr(VI) adsorption capability of the sludge sample. There were 3 replicates for each sludge samples, considering not only the test error, but also the influence of too much samples on the stable operation of the sludge system.

Results

The sludge samples, which were measured out equally from these two ASBR reactors, were used to adsorb Cr(VI) of the synthetic wastewater II, and the capability of each sample was determined, when these two ASBR systems had been running stably for 45 days. The sludge samples fetched from system A and B were named as sludge A and B, respectively. The characteristics of the sludge A and B were tested twice and the average value of each index was shown in Table 2.

Determination of the optimum adsorption time

The variation of Cr(VI) removal rates with the stirring time was shown in Fig. 2. Cr(VI) removal rates were above 98%, when the stirring time varied from 15 to 45 min, and even more than 99% Cr(VI) were removed at the stirring time of 45 min. But then Cr(VI) removal rate decreased and fluctuated with the stirring going on, for the adsorbed Cr(VI) re-dissolved into the liquid phase. Therefore, the optimum adsorption time were determined as 45 min and applied in the research.

Once continuous adsorption capacity

The solution reached adsorption equilibrium after five single adsorption periods, so a once continuous adsorption period contained five single adsorption periods in this study. The Cr(VI) residual

Table 2 Characteristics of sludge A and B used in absorption experiments ($n = 2$)

Sludge	Index				
	SV_{30} (%)	SVI ($l\ g^{-1}$)	MLSS ($g\ l^{-1}$)	Ash constituent (%)	VSS ($g\ l^{-1}$)
A	34.5	38.0	9.00	40.00	5.40
B	29.0	29.0	10.10	44.55	5.60

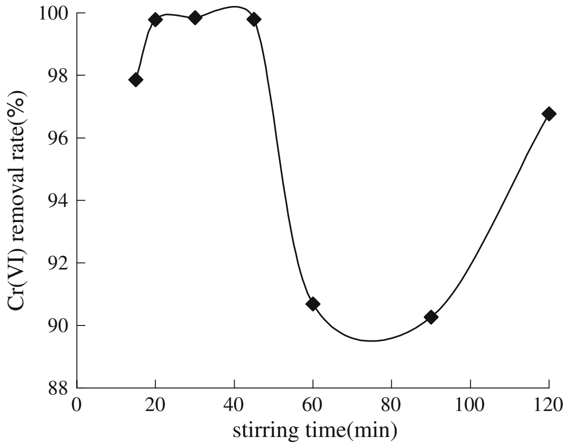

Fig. 2 The relationship between stirring time and Cr(VI) removal rate ($n = 2$)

concentrations in the liquid phase after each periods were tested, and the variety of the single adsorption capacities and the summation were shown in Fig. 3. The VSS values and other results of the testing sludge A and B were shown in Table 3.

After the first single adsorption period, Cr(VI) adsorption capacities of the sludge A and B were 9.93 and 9.79 mg, and the average Cr(VI) removal rates reached 99.3 and 97.9%, respectively. Cr(VI) adsorption capacities of both sludge samples were decreasing with the increasing of the single adsorption period, but Cr(VI) adsorption capacities of the sludge A decreased more quickly than that of the sludge B. After a once continuous adsorption period, the adsorption capacities of the sludge A and B were

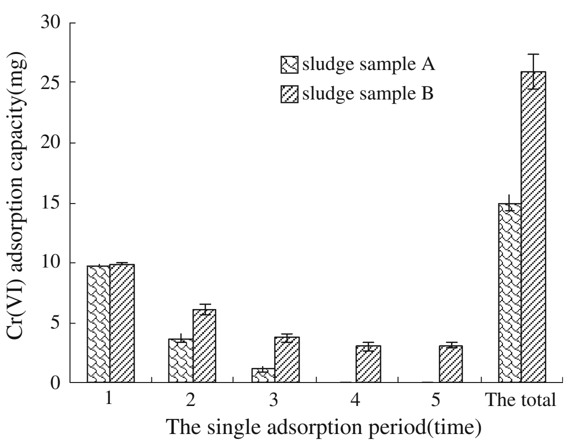

Fig. 3 The variation of the Cr(VI) adsorption capacity in a once continuous adsorption period ($n = 3$)

Table 3 Characteristics and capacities of these two adsorbed sludge samples after a once continuous adsorption experiment ($n = 3$)

Index	Sludge sample	
	A	B
VSS (g l^{-1})	4.40 (0.31)	4.65 (0.22)
Average Cr(VI) removal rate (%)	29.89	51.76
Cr(VI) removal efficiency (mg Cr(VI) g^{-1}VSS)	33.98	55.66

14.95 and 25.88 mg, the removal rates of Cr(VI) in liquid phase were 29.89 and 51.76%, and the Cr(VI) removal efficiencies were 33.98 mg Cr(VI) g^{-1}VSS and 55.66 mg Cr(VI) g^{-1}VSS, respectively. It was concluded that Cr(VI) continuous adsorption capacity of the sludge B was more than that of the sludge A by 63.82% and the weak magnetic field could improve the Cr(VI) removal rate of the activated sludge. The standard deviations of the single adsorption capacities and their summation ranged from 0 to 1.45 and all the relative standard deviations were no more than 10%, which showed a good recurrence.

Influence of regeneration on the adsorption capacity of the sludge

The results of the single adsorption-regeneration experiments and the once continuous adsorption-regeneration experiments were shown in Figs. 4 and 5, respectively. And the characteristics and capacities of the Cr(VI)-adsorbed sludge sample A and B after the single adsorption-regeneration and the once continuous adsorption-regeneration experiments were all shown in Table 4.

The results showed that the influence of the regeneration on the sludge A was much different from that of the sludge B in the single adsorption-regeneration experiment. Cr(VI) adsorption efficiency of the sludge A decreased obviously and it was nearly un-checkable in the 13th single adsorption-regeneration period. While Cr(VI) adsorption efficiencies of the sludge B were above 95% in the first 5 single adsorption-regeneration periods and there was a drop of 41.71% in the 13th period. After 13 single adsorption-regeneration periods, the Cr(VI) adsorption capacities of the sludge A and B were 70.89 and 110.15 mg, the average Cr(VI) removal rates were

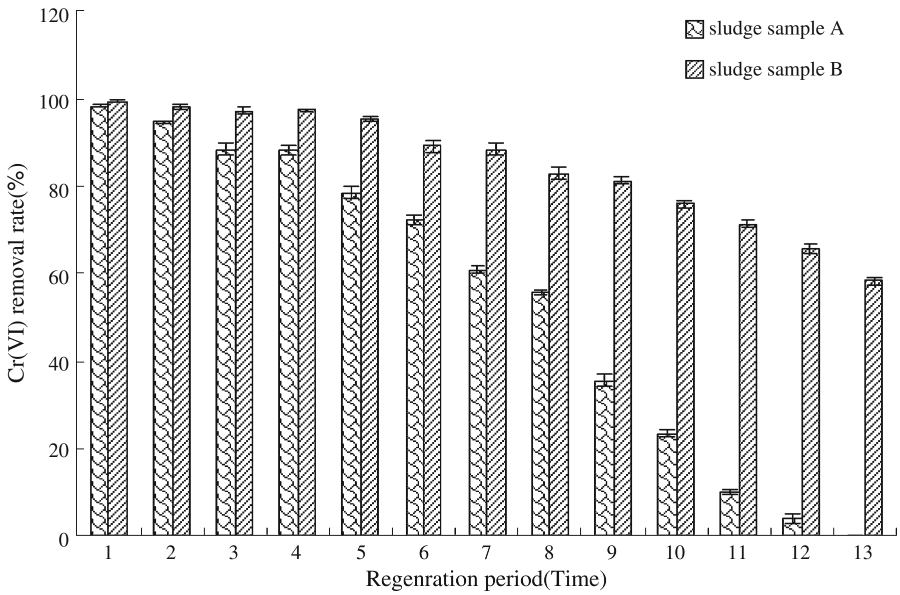

Fig. 4 Influence of the regeneration on Cr(VI) removal rate in single adsorption experiment ($n = 3$)

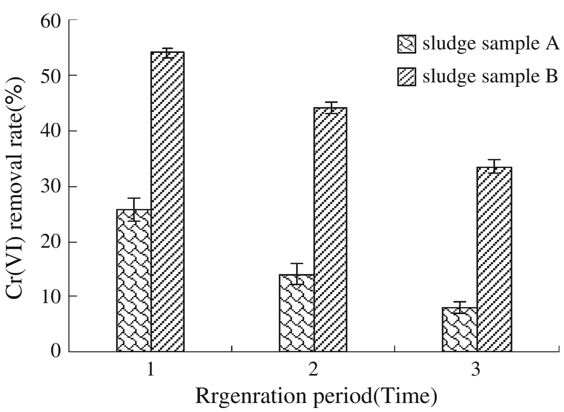

Fig. 5 Influence of the regeneration on Cr(VI) removal rate in once continuous adsorption experiment ($n = 3$)

54.53 and 84.73%, and the Cr(VI) removal efficiencies were 140.38 mg Cr(VI) g^{-1}VSS and 189.91 mg Cr(VI) g^{-1}VSS, respectively. It was concluded that Cr(VI) single adsorption-regeneration capacity of the sludge B was more than that of the sludge A by 35.26% and the weak magnetic field could improve the regeneration efficiency of the activated sludge.

The influences of the regeneration on the once continuous adsorption capacities of both samples were so limited that Cr(VI) adsorption efficiency of the sludge A and B in the third period of the once continuous adsorption-regeneration experiment decreased to 8.12 and 33.51%, respectively. And after 3 periods of the once continuous adsorption-regeneration experiments, the Cr(VI) adsorption capacities of the sludge A and B were 23.91 and 65.88 mg, the average Cr(VI) removal rates were 15.94 and 43.92%, and the Cr(VI) removal efficiencies were 59.04 mg Cr(VI) g^{-1}VSS and 131.76 mg Cr(VI) g^{-1}VSS, respectively. It was concluded that though the function of the regeneration on the sludge samples after the once continuous adsorption periods were very limited, the Cr(VI) once continuous adsorption-regeneration capacity of the sludge B was more than that of the sample A by 123.17% and the weak magnetic field could improve the effect of the regeneration on the Cr(VI) once continuous adsorption capability of the activated sludge obviously.

The standard deviations of the single adsorption-regeneration capacities and those of the once continuous adsorption-regeneration capacities ranged from 0 to 2.05 and all the relative standard deviations were no more than 8%, which showed a good recurrence. Both results of the single adsorption-regeneration experiments and the once continuous adsorption-regeneration experiments showed that the condition of the weak magnetic field did increase the Cr(VI) adsorption and regeneration efficiencies of the testing sludge, the more the total quantity of Cr(VI) was removed from the liquid phase in an operation unit, the lower

Table 4 Characteristics and capacities comparison between these two adsorbed sludge samples after adsorption-regeneration experiments ($n = 3$)

Index	Sludge sample			
	A		B	
	Single adsorption-regeneration	Once continuous adsorption-regeneration	Single adsorption-regeneration	Once continuous adsorption-regeneration
VSS ($g\ l^{-1}$)	5.05 (0.30)	4.05 (0.19)	5.80 (0.27)	5.00 (0.28)
Average Cr(VI) removal rate (%)	54.53	15.94	84.73	43.92
Cr(VI) removal efficiency (mg Cr(VI) g^{-1}VSS)	140.38	59.04	189.91	131.76

the regeneration efficiency was. So it was necessary to prolong the life of the sludge system by keeping a relative low F/M in Cr(VI) bio-removal system.

Discussion

What happen during the regeneration of the absorbed sludge?

As an effective regeneration method, leaving unused with some nutrients for 48 h could renew the Cr(VI) removal efficiency of the sludge effectively. Studies on a biotic microorganism had shown that microbial Cr(VI) removal from solutions typically included the following stages: (1) the binding of chromium to cell surfaces; (2) translocation of chromium into the cell; (3) reduction of Cr(VI) to Cr(III). Intracellular reduction of Cr(VI) to Cr(III) is known to be the main detoxification mechanism, and the reduction can take place easily when there are some organic matters in the environment. So the regeneration mode of leaving unused with a small quantity of some nutrients for 48 h just re-release the adsorption sites and decreased the toxicity of Cr(VI) by accelerating the last two steps. Compared with the control, the adsorption sites on the zoogloea of the regenerated sludge were re-released and the most removal capability of the testing sludge on Cr(VI) was renewed. The nutrient liquid could increase the activity of the sludge by accelerating the growth of the sludge microorganism and the reduction of absorbed Cr(VI). Cr(VI) were not recycled, but might transfer into the sludge or forming a steadier state, such as $Cr(OH)_3$.

What is the function of the magnetic field?

Compared with the control, the testing sludge samples fetched from the reactor B with the weak magnetic field showed higher Cr(VI) removal capacities and regeneration efficiencies, which indicated that the weak magnetic field did improve the Cr(VI) bio-removal efficiency and stability of the sludge. A great deal of researches showed that magnetized water had higher pH and electric conductivity than general tap water. In addition, magnetization could cause a higher osmotic pressure of water and stronger permeability through cell membrane (Boleslaw 1985; Lednev 1991). Direct function of some magnetic field on intracellular water and substance could activate cytoenzyme and accelerate the bio-chemical reaction in creature bodies (Liboff et al. 2003). These reports indicated that some magnetic field could improve the biological system by affecting the physical characteristics of the water and the activity of the biomacromolecule. Yavuz et al. studied the biosorption–desorption properties of magnetically modified yeast cells (bottom yeast, *Saccharomyces cerevisiae* subsp. *uvarum*) from synthetic solutions in batch system. The biosorption capacities are 29.9 mg g^{-1} for Cu^{2+}, 76.2 mg g^{-1} for Hg^{2+}, 14.1 mg g^{-1} for Ni^{2+} and 11.8 mg g^{-1} for Zn^{2+} (Yavuz et al. 2006). Tomska and Wolny found that COD removal for testing unit where the activated sludge return was exposed to magnetic field was as higher as for control unit, while the nitrification process was more effective for testing unit with magnets (Tomska and Wolny 2008). The magnetic *P. delafieldii* R-8 were used in the bioregeneration of desulfurization adsorbents Ag-Y, and the concentration of dibenzothiophene (DBT) and 2-

hydroxybiphenyl (2-HBP) with free cells is a little higher that that with magnetic cells (Li et al. 2008b). A magnetic field of 6 mT produced by a pair of permanent magnets can improve the growth of two Cr(VI) bio-removal strains and increase the Cr(VI) bio-removal efficiency (Xu and Sun 2008). These reports gave further support to the results and confirmed the physical and biological effects of magnetic field. The magnetic-biological combined technique had attracted more and more attention in the recent years and its application would certainly be improved by the results of some magnetic field effecting sludge activity and operation mode.

Conclusions

In summary, compared with the adsorption mode of the single adsorption, the mode of the once continuous adsorption could improve the Cr(VI) adsorption capacity of an operation unit, but this adsorption mode went against the regeneration of the sludge. Based on a high sludge concentration, the batch operation was a more ideal mode for the bio-removing of Cr(VI) in wastewater than the continuous adsorption. As an effective regeneration method, leaving unused with some nutrients for 48 h could renew the Cr(VI) removal efficiency of the sludge effectively. The testing sludge samples fetched from the reactor B with the weak magnetic field showed higher Cr(VI) removal capacities and regeneration efficiencies than the control, which indicated that the weak magnetic field did improve the Cr(VI) bio-removal efficiency and stability of the sludge. All the relative standard deviations of all the Cr(VI) adsorption capacities measured in the study were no more than 10%, which showed a good recurrence. The results presented here will be useful in application of the magnetic-biological combined technique in wastewater treatment.

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